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## IV.E.3 Activation of Hydrogen under Ambient Conditions by Main Group Molecules

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### Program Scope

The main theme of this project is the investigation of the reactions of small, important molecules such as hydrogen, olefins, alkanes, amines, isocyanides, carbon monoxide, carbon dioxide, and related species, with main group element compounds. The reactivity of the compounds arises from the presence of both occupied and unoccupied frontier orbitals, which are separated by modest energies of four electron volts or less. The reactions generally occur by a synergic route that involves a push-pull redistribution of electron density that facilitates bond making and breaking. The conditions for reaction reversibility are determined by the energy and symmetry of the molecular energy levels in the compounds, which can be manipulated by changing the electronic and steric properties of the substituents. In principle, the information from these studies can be used to design inexpensive catalysts for fundamental organometallic reactions based on earth-abundant elements, rather than on rare and expensive noble metals. The major focus is on compounds of the elements silicon and aluminum, which are the second and third most abundant elements in the earth's crust. Unfortunately, there are few stable low-coordinate silicon and aluminum compounds with suitable frontier orbital properties for reversible small molecule binding. A program is underway to synthesize low-valent and/or small molecular clusters of these elements with reactive exposed atoms. In the clusters, the coordination of their constituent elements can resemble that of the surfaces of the pure elements, which generally possess highly reactive surface atoms that interact readily with small molecules. The clusters also offer multiple coordination sites for synergistic reactions.

### FY 2014 Highlights

Over the past year, work has concerned a variety of topics relevant to the project's theme. The first reversible complexation of ethylene by a silylene under ambient conditions was studied and the energetics of the reaction were determined. It was shown that the silylene also reacted readily with a variety of substituted alkynes, but not with substituted alkenes, except for conjugated alkenes. A diarylgermylene was shown to react reversibly with white phosphorus at room temperature. A cage germanium-phosphorus compound was formed and characterized spectroscopically and structurally. Photolysis in toluene resulted in regeneration of the germylene and phosphorus. It was shown that the reaction cycle could be repeated up to ten times with little decomposition. In addition, diarylgermylene or stannylene was shown to insert readily into a phosphorus-hydrogen bond of phosphine to generate primary phosphide products. In anticipation of their use as synthons, four bulky primary organoalanes were synthesized and characterized. They were shown to react with ammonia and phosphine to give primary amido alanes or cages with aluminum-phosphorus frameworks. The primary alanes were also reacted with alkenes and alkynes. The latter readily underwent a cis-addition to the Al-H moiety under mild conditions. The ready addition to both terminal olefins and alkynes was attributed to the bulky aluminum substituent, which generated high concentrations of the more reactive unassociated alane. An inverse relationship between the size of the alane substituent and reactivity was established experimentally. The reaction of methylisocyanide with a diarylgermylene afforded isocyanide coupling/oligomerization through carbon-carbon bond formation. Investigation of the reaction mechanism showed that the initial step involved isocyanide complexation, followed by sequential migratory insertion into the germanium-carbon bond and subsequent carbon-hydrogen bond activation.